

WO 00/27354

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PCT/EP99/08286

Utilization of Cation-active Mixtures

Field of the Invention

This invention relates generally to cationic surfactants and, more particularly, to the use of oil-containing cosmetic preparations containing esterquats, fatty alcohols and fatty alcohol polyglycol ethers.

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~~Priority Art~~

Cationic surfactants of the esterquat type have been used for some time for hair conditioning cosmetics. By virtue of their favorable sensorial properties, these compounds are also being increasingly used in skin cosmetics. However, cosmetic emulsions containing known esterquats as conditioning agents or cationic emulsifiers, are not entirely satisfactory from the performance point of view. For example consumers complain that the emulsions leave an oily residue behind, do not spread quickly enough and should be absorbed more quickly.

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Reference is made in this connection to German patent **DE-C1 4308794** (Henkel) which describes a process for the production of solid esterquats in which the quaternization of triethanolamine esters is carried out in the presence of suitable dispersants, preferably fatty alcohols; these preparations are used as hair conditioners. In addition, according to **DE-C1 4335782** (Henkel), the quaternization of triethanolamine fatty acid esters is carried out in the presence of polyols, for example glycerol, ethylene glycol, partial glycerides, nonionic surfactants and the like, in order to avoid the use of inflammable isopropyl alcohol as solvent.

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Accordingly, the problem addressed by the present invention was to provide oil-containing cosmetic preparations containing cationic surfactants of the esterquat type which would be distinguished by improved sensorial properties and, in particular, by quick spreading and rapid residue-free absorption.

Description of the Invention

The present invention relates to the use of cationic mixtures containing

- (a) esterquats,
- (b) oil components,
- (c) fatty alcohols and
- (d) fatty alcohol polyglycol ethers

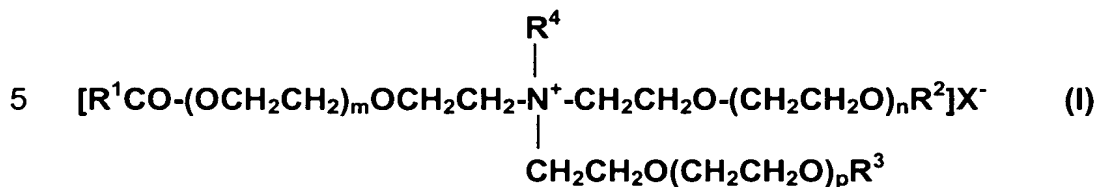
for the production of skin-cleansing and skin-care preparations.

It has surprisingly been found that oil-containing skin-cleansing and skin-care preparations, preferably in emulsion form, which contain esterquats together with fatty alcohols and fatty alcohol polyglycol ethers, preferably mixtures of cetearyl alcohol and cetearyl ethoxylates, provide the skin with a particularly pleasant feel, do not leave any residues behind, spread quickly and are rapidly absorbed.

Esterquats

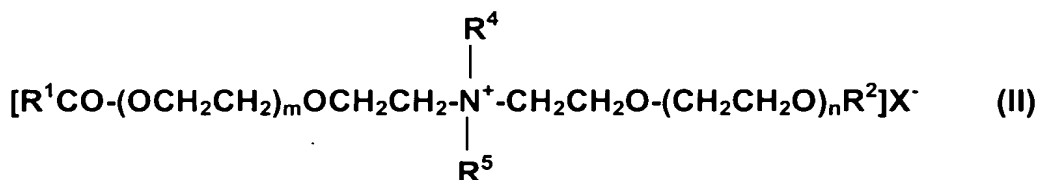
"Esterquats" are generally understood to be quaternized fatty acid triethanolamine ester salts. These are known substances which may be obtained by the relevant methods of preparative organic chemistry, cf. International patent application WO 91/01295 (Henkel). According to this document, triethanolamine is partly esterified with fatty acids in the presence of hypophosphorous acid, air is passed through and the reaction product is quaternized with dimethyl sulfate or ethylene oxide. Overviews on this subject have been published, for example, by R. Puchta et al. in **Tens. Surf. Det.**, 30, 186 (1993), by M. Brock in **Tens. Surf. Det.** 30, 394 (1993), by R. Lagerman et al. in **J. Am. Oil. Chem. Soc.**, 71, 97 (1994) and by I. Shapiro in **Cosm. Toil**, 109, 77 (1994).

The esterquats which form component (a) correspond, for example, to formula (I):

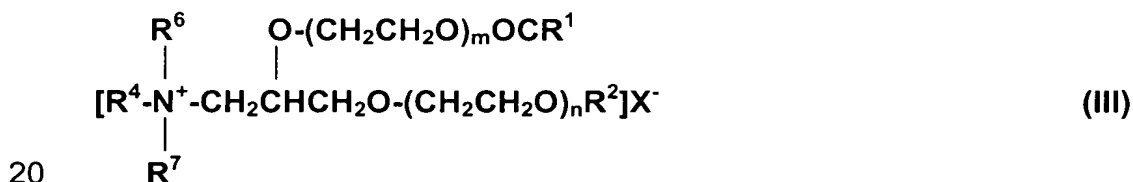


in which R^1CO is an acyl group containing 6 to 22 carbon atoms and preferably 12 to 18 carbon atoms, R^2 and R^3 independently of one another represent hydrogen or have the same meaning as R^1CO , R^4 is an alkyl group containing 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group, m , n and p together stand for 0 or numbers of 1 to 12, q is a number of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate. To produce the quaternized esters, the fatty acids, for example palm oil fatty acid, coconut oil fatty acid or tallow fatty acid, and the triethanolamine may be used in a molar ratio of 1.1:1 to 3:1. With the performance properties of the esterquats in mind, a ratio of 1.2:1 to 2.2:1 and preferably 1.5:1 to 1.9:1 has proved to be particularly advantageous. The preferred esterquats are technical mixtures of mono-, di- and triesters with an average degree of esterification of 1.5 to 1.9 and are derived from technical $C_{12/18}$ palm oil fatty acid (iodine value 0 to 40). In performance terms, quaternized fatty acid triethanolamine ester salts corresponding to formula (I), in which R^1CO is a palm acyl group containing 12 to 18 carbon atoms, R^2 has the same meaning as R^1CO , R^3 is hydrogen, R^4 is a methyl group, m , n and p stand for 0 and X stands for methyl sulfate, have proved to be particularly advantageous.

Another group of suitable esterquats are quaternized ester salts of the fatty acids mentioned with diethanolalkylamines corresponding to formula (II):



in which R^1CO is an acyl group containing 6 to 22 carbon atoms and preferably 12 to 18 carbon atoms, R^2 is hydrogen or has the same meaning as R^1CO , R^4 and R^5 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X stands for halide, alkyl sulfate or alkyl phosphate. Finally, another group of suitable esterquats are the quaternized ester salts of the fatty acids mentioned with 1,2-dihydroxypropyl dialkylamines corresponding to formula (III):



in which R^1CO is an acyl group containing 6 to 22 carbon atoms and preferably 12 to 18 carbon atoms, R^2 is hydrogen or has the same meaning as R^1CO , R^4 , R^6 and R^7 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X stands for halide, alkyl sulfate or alkyl phosphate. So far as the choice of the optimum degree of esterification is concerned, the examples mentioned in regard to (I) also apply to the esterquats of formulae (II) and (III).

Oil components

Suitable oil components are, for example, Guerbet alcohols based on fatty alcohols containing 6 to 18 and preferably 8 to 10 carbon atoms,

esters of linear C₆₋₂₂ fatty acids with linear C₆₋₂₂ fatty alcohols, esters of branched C₆₋₁₃ carboxylic acids with linear C₆₋₂₂ fatty alcohols, esters of linear C₆₋₂₂ fatty acids with branched alcohols, more particularly 2-ethyl hexanol, esters of hydroxycarboxylic acids with linear or branched C₆₋₂₂ fatty alcohols, more especially Dioctyl Malate, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, triglycerides based on C₆₋₁₀ fatty acids, liquid mono-/di-/triglyceride mixtures based on C₆₋₁₈ fatty acids, esters of C₆₋₂₂ fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, more particularly benzoic acid, esters of C₂₋₁₂ dicarboxylic acids with linear or branched alcohols containing 1 to 22 carbon atoms or polyols containing 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear and branched C₆₋₂₂ fatty alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C₆₋₂₂ alcohols (for example Finsolv® TN), linear or branched, symmetrical or nonsymmetrical dialkyl ethers containing 6 to 22 carbon atoms per alkyl group, ring opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons.

Fatty alcohols and fatty alcohol polyglycol ethers

Fatty alcohols in the context of the invention are primary, preferably long-chain and linear alcohols which typically correspond to formula (IV):



in which R⁸ is a linear or branched alkyl or alkenyl group containing 6 to 22 carbon atoms. Typical examples are caproic alcohol, caprylic alcohol, capric alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, erucyl alcohol, behenyl alcohol and the technical mixtures

obtained in the pressure hydrolysis of natural triglycerides. The fatty alcohol polyglycol ethers preferably correspond to formula (V):



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in which R^9 is a linear or branched alkyl and/or alkenyl group containing 6 to 22 carbon atoms and n is a number of 1 to 20. They may be products of the addition of 1 to 20 and preferably 10 to 15 moles ethylene oxides onto the above-mentioned fatty alcohols; the ethoxylates may have both a conventional broad homolog distribution and a narrow homolog distribution. It has proved to be of advantage for fatty alcohols and polyglycol ethers to have the same fatty residue. Cetearyl alcohol, a 1:1 mixture of cetyl and stearyl alcohol, and adducts of 1 to 20 and preferably 10 to 15 moles ethylene oxide with cetearyl alcohol are preferably used. Mixtures of components (a), (c) and (d) which are obtained as technical mixtures through the production process used are also preferred. To this end, alkanolamine fatty acid esters are reacted with alkylating agents in the presence of such quantities of fatty alcohol and fatty alcohol polyglycol ethers, preferably mixtures of cetearyl alcohol and cetearyl polyglycol ethers, that a ratio by weight of esterquat to fatty alcohol/fatty alcohol polyglycol ether of 90:10 to 10:90 and preferably 80:20 to 70:30 or 20:80 to 30:70 is obtained. The esterification and quaternization may be carried out in known manner, as fully described, for example, in **DE-C1 4308794** and **DE-C1 4335782** (Henkel). The particular advantage of using such mixtures is that they are easy to disperse, even without heating. Surprisingly, these directly prepared binary mixtures are also sensorially superior to the mixture of individual components in the formulation.

Cosmetic preparations

As mentioned at the beginning, the cosmetic preparations according

to the present invention are normally emulsions which may be both w/o and o/w emulsions; multiple emulsions of the w/o/w or o/w/o type are also suitable. In one preferred embodiment of the invention, the preparations may have the following composition:

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- (a) 0.1 to 25, preferably 5 to 15% by weight of esterquats,
- (b) 0.5 to 90, preferably 5 to 50% by weight of oil components,
- (c) 0.1 to 75, preferably 5 to 50% by weight of fatty alcohols and
- (d) 0.1 to 75, preferably 5 to 50% by weight alcohol polyglycol ethers,

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with the proviso that the quantities shown add up to 100% by weight with water and optionally other ingredients.

Commercial Applications

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The preparations according to the invention, for example hair aftertreatments, hair conditioners, hair coloring emulsions, body washes and body-care products, sun protection creams, lotions and ointments and make-up and other decorative cosmetic products, may also contain mild surfactants, emulsifiers, superfatting agents, pearlizing waxes, stabilizers, consistency factors, thickeners, polymers, silicone compounds, biogenic agents, deodorants, antidandruff agents, film formers, preservatives, hydrotropes, solubilizers, UV protection factors, antioxidants, insect repellents, self-tanning agents, perfume oils, dyes and the like as further auxiliaries and additives.

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Typical examples of suitable mild, i.e. particularly dermatologically compatible, **surfactants** are fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or dialkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, ether carboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines and/or protein fatty acid condensates,

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preferably based on wheat proteins.

Suitable **emulsifiers** are, for example, nonionic surfactants from at least one of the following groups:

- 5 (1) products of the addition of 2 to 30 moles ethylene oxide and/or 0 to 5 moles propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group;
- 10 (2) C_{12/18} fatty acid monoesters and diesters of products of the addition of 1 to 30 moles ethylene oxide onto glycerol;
- (3) glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide adducts thereof;
- 15 (4) alkyl mono- and oligoglycosides containing 8 to 22 carbon atoms in the alkyl group and ethoxylated analogs thereof;
- (5) adducts of 15 to 60 moles ethylene oxide with castor oil and/or hydrogenated castor oil;
- (6) polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate, polyglycerol poly-12-hydroxy-
20 stearate and polyglycerol dimerate. Mixtures of compounds from several of these classes are also suitable;
- (7) products of the addition of 2 to 15 moles ethylene oxide onto castor oil and/or hydrogenated castor oil;
- 25 (8) partial esters based on linear, branched, unsaturated or saturated C_{6/22} fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);
- 30 (9) mono-, di- and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl

phosphates and salts thereof;

(10) wool wax alcohols;

(11) polysiloxane/polyalkyl polyether copolymers and corresponding derivatives;

5 (12) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol according to **DE-PS 1165574** and/or mixed esters of fatty acids containing 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol, and

(13) polyalkylene glycols.

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The addition products of ethylene oxide and/or propylene oxide with fatty alcohols, fatty acids, glycerol monoesters and diesters and sorbitan monoesters and diesters of fatty acids or with castor oil are known commercially available products. They are homolog mixtures of which the
15 average degree of alkoxylation corresponds to the ratio between the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. $C_{12/18}$ fatty acid monoesters and diesters of adducts of ethylene oxide with glycerol are known as refatting agents for cosmetic formulations from **DE-PS 20 24 051**.

20 $C_{8/18}$ alkyl mono- and oligoglycosides, their production and their use are known from the prior art. They are produced in particular by reacting glucose or oligosaccharides with primary alcohols containing 8 to 18 carbon atoms. So far as the glucoside unit is concerned, both monoglycosides in which a cyclic sugar unit is attached to the fatty alcohol
25 by a glycoside bond and oligomeric glycosides with a degree of oligomerization of preferably up to about 8 are suitable. The degree of oligomerization is a statistical mean value on which the homolog distribution typical of such technical products is based.

Other suitable emulsifiers are zwitterionic surfactants. Zwitterionic
30 surfactants are surface-active compounds which contain at least one

quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of *Cocamidopropyl Betaine* is particularly preferred. Ampholytic surfactants are also suitable emulsifiers. Ampholytic surfactants are surface-active compounds which, in addition to a C_{8/18} alkyl or acyl group, contain at least one free amino group and at least one -COOH- or -SO₃H- group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and C_{12/18} acyl sarcosine. Besides ampholytic emulsifiers, quaternary emulsifiers may also be used, those of the esterquat type, preferably methyl-quaternized difatty acid triethanolamine ester salts, being particularly preferred.

Superfatting agents may be selected from such substances as, for example, lanolin and lecithin and also polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the fatty acid alkanolamides also serving as foam stabilizers.

Suitable **pearlizing waxes** are, for example, alkylene glycol esters,

especially ethylene glycol distearate; fatty acid alkanolamides, especially cocofatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polybasic, optionally hydroxysubstituted carboxylic acids with fatty alcohols containing 6 to 22 carbon atoms, especially long-chain esters of tartaric acid; fatty compounds, such as for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates which contain in all at least 24 carbon atoms, especially laurone and distearylether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring opening products of olefin epoxides containing 12 to 22 carbon atoms with fatty alcohols containing 12 to 22 carbon atoms and/or polyols containing 2 to 15 carbon atoms and 2 to 10 hydroxyl groups and mixtures thereof.

The **consistency factors** mainly used are fatty alcohols or hydroxyfatty alcohols containing 12 to 22 and preferably 16 to 18 carbon atoms and also partial glycerides, fatty acids or hydroxyfatty acids. A combination of these substances with alkyl oligoglucosides and/or fatty acid N-methyl glucamides of the same chain length and/or polyglycerol poly-12-hydroxystearates is preferably used. Suitable **thickeners** are, for example, polysaccharides, more especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, also relatively high molecular weight polyethylene glycol monoesters and diesters of fatty acids, polyacrylates (for example Carbopols® [Goodrich] or Synthalens® [Sigma]), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols, for example pentaerythritol or trimethylol propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes, such as sodium chloride and ammonium chloride.

Suitable **cationic polymers** are, for example, cationic cellulose derivatives such as, for example, the quaternized hydroxyethyl cellulose

obtainable from Amerchol under the name of Polymer JR 400®, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinyl pyrrolidone/vinyl imidazole polymers such as, for example, Luviquat® (BASF), condensation products of polyglycols and amines, quaternized collagen polypeptides such as, for example, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen (Lamequat® L, Grünau), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers such as, for example, amodimethicone, copolymers of adipic acid and dimethylaminohydroxypropyl diethylenetriamine (Cartaretine®, Sandoz), copolymers of acrylic acid with dimethyl diallyl ammonium chloride (Merquat® 550, Chemviron), polyaminopolyamides as described, for example, in **FR-A 2 252 840** and crosslinked water-soluble polymers thereof, cationic chitin derivatives such as, for example, quaternized chitosan, optionally in microcrystalline distribution, condensation products of dihaloalkyls, for example dibromobutane, with bis-dialkylamines, for example bis-dimethylamino-1,3-propane, cationic guar gum such as, for example, Jaguar® CBS, Jaguar® C-17, Jaguar® C-16 of Celanese, quaternized ammonium salt polymers such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 of Miranol.

20 Suitable **anionic, zwitterionic, amphoteric and nonionic polymers** are, for example, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinylether/maleic anhydride copolymers and esters thereof, uncrosslinked and polyol-crosslinked polyacrylic acids, 25 acrylamidopropyl trimethylammonium chloride/acrylate copolymers, octylacrylamide/methyl methacrylate/tert.-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, vinyl pyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and optionally derivatized 30 cellulose ethers and silicones.

Suitable **silicone compounds** are, for example, dimethyl polysiloxanes, methylphenyl polysiloxanes, cyclic silicones and amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds which may be both liquid and resin-like at room
5 temperature. A detailed overview of suitable volatile silicones can be found in Todd et al. in **Cosm. Toil.** 91, 27 (1976).

Typical examples of **fats** are glycerides while suitable **waxes** are inter alia beeswax, carnauba wax, candelilla wax, montan wax, paraffin wax or microwaxes, optionally in combination with hydrophilic waxes, for
10 example cetyl stearyl alcohol or partial glycerides. Metal salts of fatty acids such as, for example, magnesium, aluminium and/or zinc stearate or ricinoleate may be used as **stabilizers**.

In the context of the invention, **biogenic agents** are, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid,
15 deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes.

Suitable **deodorizers** are, for example, antiperspirants, such as aluminium chlorohydrates. These antiperspirants are colorless
20 hygroscopic crystals which readily deliquesce in air and which accumulate when aqueous aluminium chloride solutions are concentrated by evaporation. Aluminium chlorohydrate is used for the production of perspiration-inhibiting and deodorizing formulations and probably acts by partially blocking the sweat glands through the precipitation of proteins
25 and/or polysaccharides [cf. **J. Soc. Cosm. Chem.** 24, 281 (1973)]. For example, an aluminium chlorohydrate which corresponds to the formula $[Al_2(OH)_5Cl] \cdot 2.5H_2O$ and which is particularly preferred for the purposes of the invention is commercially available under the name of Locron® from Hoechst AG of Frankfurt, FRG [cf. **J. Pharm. Pharmacol.** 26, 531 (1975)].
30 Besides the chlorohydrates, aluminium hydroxylactates and acidic

aluminium/zirconium salts may also be used. Other suitable deodorizers are esterase inhibitors, preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and, in particular, triethyl citrate (Hydagen® CAT, Henkel KGaA, Düsseldorf, FRG). Esterase inhibitors inhibit enzyme activity and thus reduce odor formation. The free acid is probably released through the cleavage of the citric acid ester, reducing the pH value of the skin to such an extent that the enzymes are inhibited. Other esterase inhibitors are dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester, hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial agents which influence the germ flora and destroy or inhibit the growth of perspiration-decomposing bacteria, may also be present in stick products. Examples of such antibacterial agents are chitosan, phenoxyethanol and chlorhexidine gluconate. 5-Chloro-2-(2,4-dichlorophenoxy)-phenol, which is marketed under the name of Irgasan® by Ciba-Geigy of Basel, Switzerland, has also proved to be particularly effective.

Suitable **antidandruff agents** are climbazol, octopirox and zinc pyrithione. Standard **film formers** are, for example, chitosan, microcrystalline chitosan, quaternized chitosan, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof and similar compounds. Suitable **swelling agents** for aqueous phases are montmorillonites, clay minerals, Pemulen and alkyl-modified Carbopol types (Goodrich). Other suitable polymers and swelling agents can be found in R. Lochhead's review in **Cosm. Toil.** 108, 95 (1993).

UV protection factors in the context of the invention are, for example, organic substances (UV filters) which are liquid or crystalline at

room temperature and which are capable of absorbing ultraviolet radiation and of releasing the energy absorbed in the form of longer-wave radiation, for example heat. UV-B filters can be oil-soluble or water-soluble. The following are examples of oil-soluble substances:

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- 3-benzylidene camphor or 3-benzylidene norcamphor and derivatives thereof, for example 3-(4-methylbenzylidene)-camphor as described in **EP-B1 0693471**;

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- 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino)-benzoic acid-2-ethylhexyl ester, 4-(dimethylamino)-benzoic acid-2-octyl ester and 4-(dimethylamino)-benzoic acid amyl ester;

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- esters of cinnamic acid, preferably 4-methoxycinnamic acid-2-ethylhexyl ester, 4-methoxycinnamic acid propyl ester, 4-methoxycinnamic acid isoamyl ester, 2-cyano-3,3-phenylcinnamic acid-2-ethylhexyl ester (Octocrylene);

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- esters of salicylic acid, preferably salicylic acid-2-ethylhexyl ester, salicylic acid-4-isopropylbenzyl ester, salicylic acid homomenthyl ester;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;

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- esters of benzalmalonic acid, preferably 4-methoxybenzalmalonic acid di-2-ethylhexyl ester;
- triazine derivatives such as, for example, 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and Octyl Triazone as described in **EP-A1 0818450**;
- propane-1,3-diones such as, for example, 1-(4-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione;
- ketotricyclo(5.2.1.0)decane derivatives as described in **EP-B1 0694521**.

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Suitable water-soluble substances are

- 2-phenylbenzimidazole-5-sulfonic acid and alkali metal, alkaline earth metal, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
- 5 • sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and salts thereof;
- sulfonic acid derivatives of 3-benzylidene camphor such as, for example, 4-(2-oxo-3-bornylidenemethyl)-benzene sulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)-sulfonic acid and salts thereof.

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Typical UV-A filters are, in particular, derivatives of benzoyl methane such as, for example 1-(4'-tert.butylphenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione, 4-tert.butyl-4'-methoxydibenzoyl methane (Parsol 1789) or 1-phenyl-3-(4'-isopropylphenyl)-propane-1,3-dione. The UV-A and UV-B
15 filters may of course also be used in the form of mixtures. Besides the soluble substances mentioned, insoluble light-blocking pigments, i.e. finely dispersed metal oxides or salts, for example titanium dioxide, zinc oxide, iron oxide, aluminium oxide, cerium oxide, zirconium oxide, silicates (talcum), barium sulfate and zinc stearate, may also be used for this
20 purpose. The particles should have a mean diameter of less than 100 nm, preferably between 5 and 50 nm and more preferably between 15 and 30 nm. They may be spherical in shape although ellipsoidal particles or other non-spherical particles may also be used. Other suitable UV filters can be found in P. Finkel's review in **SÖFW-Journal 122, 543 (1996)**.

25 Besides the two groups of primary sun protection factors mentioned above, secondary sun protection factors of the **antioxidant** type may also be used. Secondary sun protection factors of the antioxidant type interrupt the photochemical reaction chain which is initiated when UV rays penetrate into the skin. Typical examples are amino acids (for example glycine,
30 histidine, tyrosine, tryptophane) and derivatives thereof, imidazoles (for

example urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (for example anserine), carotinoids, carotenes (for example α -carotene, β -carotene, lycopene) and derivatives thereof, chlorogenic acid and derivatives thereof, liponic acid and derivatives thereof (for example dihydroliponic acid), aurothioglucose, propylthiouracil and other thiols (for example thioredoxine, glutathione, cysteine, cystine, cystamine and glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ -linoleyl, cholesteryl and glyceryl esters thereof) and their salts, dilaurylthiodipropionate, distearylthiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulfoximine compounds (for example butionine sulfoximines, homocysteine sulfoximine, butionine sulfones, penta-, hexa- and hepta-thionine sulfoximine) in very small compatible dosages (for example pmole to μ mole/kg) also (metal) chelators (for example α -hydroxyfatty acids, palmitic acid, phytic acid, lactoferrine), α -hydroxy acids (for example citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (for example γ -linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives thereof (for example ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (for example vitamin E acetate), vitamin A and derivatives (vitamin A palmitate) and coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, α -glycosyl rutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiac resin acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, Superoxid-Dismutase, zinc and derivatives thereof (for example ZnO, ZnSO₄),

selenium and derivatives thereof (for example selenium methionine), stilbenes and derivatives thereof (for example stilbene oxide, trans-stilbene oxide) and derivatives of these active substances suitable for the purposes of the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids).

In addition, **hydrotropes**, for example ethanol, isopropyl alcohol or polyols, may be used to improve flow behavior. Suitable polyols preferably contain 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are

- glycerol;
- alkylene glycols such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and polyethylene glycols with an average molecular weight of 100 to 1000 dalton;
- technical oligoglycerol mixtures with a degree of self-condensation of 1.5 to 10 such as, for example, technical diglycerol mixtures with a diglycerol content of 40 to 50% by weight;
- methylol compounds such as, in particular, trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- lower alkyl glucosides, particularly those containing 1 to 8 carbon atoms in the alkyl group, for example methyl and butyl glucoside;
- sugar alcohols containing 5 to 12 carbon atoms, for example sorbitol or mannitol,
- sugars containing 5 to 12 carbon atoms, for example glucose or sucrose;
- aminosugars, for example glucamine.

Suitable **preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid and the other

classes of compounds listed in Appendix 6, Parts A and B of the Kosmetikverordnung ("Cosmetics Directive"). Suitable **insect repellents** are N,N-diethyl-m-toluamide, pentane-1,2-diol or Insect Repellent 3535. A suitable **self-tanning agent** is dihydroxyacetone.

- 5 Suitable **perfume oils** are mixtures of natural and synthetic perfumes. Natural perfumes include the extracts of blossoms (lily, lavender, rose, jasmine, neroli, ylang-ylang), stems and leaves (geranium, patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peel (bergamot, lemon, orange), roots (nutmeg, angelica, celery, cardamon, costus, iris, calmus), woods (pinewood, sandalwood, guaiac wood, cedarwood, rosewood), herbs and grasses (tarragon, lemon grass, sage, thyme), needles and branches (spruce, fir, pine, dwarf pine), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials, for example civet and beaver, may also be used. Typical
- 10 synthetic perfume compounds are products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Examples of perfume compounds of the ester type are benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexylacetate, linalyl acetate, dimethyl benzyl carbonyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethylmethyl phenyl
- 15 glycinate, allyl cyclohexyl propionate, styryl propionate and benzyl salicylate. Ethers include, for example, benzyl ethyl ether while aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilyal and bourgeonal. Examples of suitable ketones are
- 20 the ionones, α -isomethylionone and methyl cedryl ketone. Suitable alcohols are anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and terpineol. The hydrocarbons mainly include the terpenes and balsams. However, it is preferred to use mixtures of different perfume compounds which, together, produce an agreeable perfume.
- 25 Other suitable perfume oils are essential oils of relatively low volatility
- 30

which are mostly used as aroma components. Examples are sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime-blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavendin oil. The following are preferably used either individually or in

- 5 the form of mixtures: bergamot oil, dihydromyrcenol, lilial, lylal, citronellol, phenylethyl alcohol, α -hexylcinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, Boisambrene Forte, Ambroxan, indole, hedione, sandelice, citrus oil, mandarin oil, orange oil, allylamyl glycolate, cyclovertal, lavendin oil, clary oil, β -damascone, geranium oil bourbon,
- 10 cyclohexyl salicylate, Vertofix Coeur, Iso-E-Super, Fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat.

Suitable **dyes** are any of the substances suitable and approved for cosmetic purposes as listed, for example, in the publication "**Kosmetische**

15 **Färbemittel**" of the **Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pages 81 to 106.** These dyes are normally used in concentrations of 0.001 to 0.1% by weight, based on the mixture as a whole.

The total percentage content of auxiliaries and additives may be

20 from 1 to 50% by weight and is preferably from 5 to 40% by weight, based on the particular composition. The compositions may be produced by standard cold and hot methods and are preferably produced by the phase inversion temperature method.

25 **Examples**

Table 1. Cosmetic preparations (water, preservative to 100% by weight)

Composition (INCI)	1	2	3	4	5	6	7	8	9	10
Texapon® NSO Sodium Laureth Sulfate	-	30.0	-	-	25.0	-	-	-	-	-
Plantacare® 818 Coco Glucosides	-	10.0	30.0	-	20.0	-	-	-	-	-
Plantacare® PS 10 Sodium Laureth Sulfate (and) Coco Glucosides	22.0	-	-	22.0	-	-	-	-	-	-
Dehyquart® C 4046 Dipalmyl Methyl Triethanol-ammonium Methosulfate (and) Cetearyl Alcohol (and) Ceteareth-10	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dehyton® PK 45 Cocamidopropyl Betaine	15.0	10.0	10.0	15.0	20.0	-	-	-	-	-
Emulgade® SE Glyceryl Stearate (and) Ceteareth 12/20 (and) Cetearyl Alcohol (and) Cetyl Palmitate	-	-	-	-	-	5.0	5.0	-	5.0	-
Eumulgin® B1 Ceteareth-12	-	-	15.0	-	-	-	-	-	-	-
Eumulgin® HRE 60 PEG 60 Hydrogenated Castor Oil	-	-	-	-	5.0	-	-	-	-	-
Lameform® TGI Polyglyceryl-3 Isostearate	-	-	-	-	-	-	-	4.0	-	-
Dehymuls® PGPH Polyglyceryl-2 Dipolyhydroxystearate	-	-	3.8	-	-	-	-	-	-	4.0
Monomuls® 90-O 18 Glyceryl Oleate	-	-	-	-	-	-	-	2.0	-	2.0
Cetiol® HE PEG-7 Glyceryl Cocoate	2.0	-	-	2.0	5.0	-	-	-	-	-
Cetiol® OE Dicaprylyl Ether	-	-	-	-	-	-	-	5.0	-	5.0
Cetiol® PGL Hexyldecanol (and) Hexyldecyl Laurate	-	-	-	-	-	-	-	10.0	3.0	10.0
Cetiol® SN Cetearyl Isononanoate	-	-	-	-	-	3.0	3.0	-	-	-
Cetiol® V Decyl Oleate	-	-	5.0	-	-	3.0	3.0	-	3.0	-
Myritol® 318 Coco Caprylate Caprate	-	-	-	-	-	-	-	5.0	-	5.0
Bees Wax	-	-	-	-	-	-	-	7.0	-	7.0
Nutrilan® Keratin W Hydrolyzed Keratin	-	-	-	-	-	40.0	60.0	-	60.0	-
Lamesoft® LMG Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collagen	-	4.0	-	-	2.0	-	-	-	-	-
Gluadin® WK Sodium Cocoyl Hydrolyzed Wheat Protein	2.0	2.0	4.0	2.0	5.0	-	-	5.0	-	5.0
Euperlan® PK 3000 AM Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	5.0	-	-	5.0	-	-	-	-	-	-
Arlypon® F Laureth-2	-	-	1.5	-	-	-	-	-	-	-
Glycerin (86% by weight)	-	-	-	-	-	3.0	3.0	5.0	3.0	5.0

(1-5) foam bath, (6) soft sream, (7,9) moisturizing emulsion, (8,10) night cream

Table 1 Cosmetic preparations (water, preservative to 100% by weight) - continued

Composition (INCI)	11	12	13	14	15	16	17	18	19	20
Dehymuls® PGPH Polyglyceryl-2 Dipolyhydroxystearate	2.0	3.0	-	5.0	-	-	-	-	-	-
Lameform® TGI Polyglyceryl-3 Diisostearate	4.0	1.0	-	-	-	-	-	-	-	-
Emulgade® PL 68/50 Cetearyl Glucoside (and) Cetearyl Alcohol	-	-	-	-	4.0	-	-	-	3.0	-
Eumulgin® B2 Ceteareth-20	-	-	-	-	-	-	-	2.0	-	-
Tegocare® PS Polyglyceryl-3 Methylglucose Distearate	-	-	-	-	-	-	4.0	-	-	-
Eumulgin VL 75 Polyglyceryl-2 Dipolyhydroxystearate (and) Lauryl Glucoside (and) Glycerin	-	-	-	-	-	3.5	-	-	2.5	-
Bees Wax	3.0	2.0	5.0	2.0	-	-	-	-	-	-
Cutina® GMS Glyceryl Stearate	-	-	-	-	-	2.0	4.0	-	-	4.0
Lanette® O Cetearyl Alcohol	-	-	2.0	-	2.0	4.0	2.0	4.0	4.0	1.0
Plantaren® 818 Cocoglycerides	5.0	-	10.0	-	8.0	6.0	6.0	-	5.0	5.0
Dehyquart® C 4046 Dipalmyl Methyl Triethanolammonium Methosulfate (and) Cetearyl Alcohol (and) Ceteareth-101	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Finsolv® TN C12/15 Alkyl Benzoate	-	6.0	-	2.0	-	-	3.0	-	-	2.0
Diocetyl Carbonate	5.0	4.0	6.0	8.0	6.0	5.0	4.0	3.0	4.0	6.0
Cetiol® J 600 Oleyl Erucate	2.0	-	3.0	5.0	4.0	3.0	3.0	-	5.0	4.0
Cetiol® OE Dicaprylyl Ether	3.0	-	-	-	-	1.0	-	-	-	-
Mineral Oil	-	4.0	-	4.0	-	2.0	-	1.0	-	-
Cetiol® PGL Hexadecanol (and) Hexyldecyl Laurate	-	7.0	3.0	7.0	4.0	-	-	-	1.0	-
Panthenol / Bisabolol	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Copherol® F 1300 Tocopherol / Tocopheryl Acetate	0.5	1.0	1.0	2.0	1.0	1.0	1.0	2.0	0.5	2.0
Neo Heliopan® Hydro Sodium Phenylbenzimidazole Sulfonate	3.0	-	-	3.0	-	-	2.0	-	2.0	-
Neo Heliopan® 303 Octocrylene	-	5.0	-	-	-	4.0	5.0	-	-	10.0
Neo Heliopan® BB Benzophenone-3	1.5	-	-	2.0	1.5	-	-	-	2.0	-
Neo Heliopan® E 1000 Isoamyl p-Methoxycinnamate	5.0	-	4.0	-	2.0	2.0	4.0	10.0	-	-
Neo Heliopan® AV Octyl Methoxycinnamate	4.0	-	4.0	3.0	2.0	3.0	4.0	-	10.0	2.0
Uvinol® T 150 Octyl Triazone	2.0	4.0	3.0	1.0	1.0	1.0	4.0	3.0	3.0	3.0
Zinc Oxide	-	6.0	6.0	-	4.0	-	-	-	-	5.0
Titanium Dioxide	-	2.0	2.0	-	-	-	-	5.0	-	-
Glycerin (86% by weight)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

(11) w/o sun protection cream, (12-14) w/o sun protection lotion, (15,18,20) o/w sun protection lotion, (16,17,19) o/w sun protection cream